SCIENCE FOR CERAMIC PRODUCTION

THE ROLE OF CRYSTAL BOUNDARIES IN DIFFUSION CREEP IN OXIDE CERAMICS

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Experimental data on the effect of the size of crystals on the high-temperature deformation of ceramic oxide materials subject to a mechanical force are presented. It is demonstrated that creep is mainly implemented by the mechanism of volume diffusion of impurity or nonstoichiometric vacancies (from inner zones to a boundary).

The crystalline structure of oxide ceramics has certain specifics, which essentially differentiates them from metals and metal alloys. An oxide structure contains several sublattices made of ions of different chemical origin and size and also different values and sign of the electric charge [1]. This is due to the ionic-covalent type of bond in oxides. The higher value and directivity of bonds between cations and anions in an elementary cell is responsible for their low mobility and, accordingly, the greater rigidity of the crystal lattice. On the other hand, the structural complexity of an elementary cell, which, as a rule, contains several formula units of the respective chemical compound (i.e., a great number of ions) is the reason for the complex structure of defects responsible for plasticity (in particular, dislocations, boundaries, etc. in metals) and their slipping surfaces. As a result, the shear (cooperative) deformation mechanisms in ceramics are so retarded that deformation via diffusion processes (that is, individual ion transitions) becomes beneficial with respect to energy consumption, especially under low loads in a high-temperature range [2]. A grid of dislocations only lowers the effective viscosity of the medium by increasing the effective coefficient of self-diffusion and decreasing the energy of mobility of vacancies owing to a total increase in the lattice energy.

The study in [3] considers experimental data on the effect of crystal lattice vacancies (thermal, impurity, or nonstoichiometric) on creep in oxide ceramics. The paper specifies factors of the origin of diffusion creep in ceramics, its motive forces, and the correlation between the self-diffusion

coefficient and the vacancy diffusion coefficient via concentration and mobility. It is demonstrated that the processes of vacancy formation (disordering) can be described using the quasichemical approach [4, 5], which implies an arbitrary division of vacancies into zones of diluted, concentrated, or saturated vacancy solutions in the matrix lattice of the host compound.

The energy of vacancy formation in diluted solutions with a low weight content of heterovalent impurities (up to about 1%) is determined by internal thermal disordering, in particular, the Schottky effect. The creep rate in this case exceeds the rate in a hypothetical impurity-free stoichiometric crystal proportionally to the concentration of defects, and the activation energy of creep is the sum of energies of vacancy formation and mobility of vacancies. The behavior of more concentrated solutions is determined by impurity centers, whose quantity determines the vacancy concentration. The activation energy of creep in this range, as the impurity concentration increases, drops to the energy of mobility of vacancies. In the range of saturated solutions, the creep rate and the activation energy are constant, since even when the content of impurities increases, the number of vacancies does not change (the concentration of the solution is constant), and activation energy corresponds to the energy of mobility of vacancies. The formation of a second crystalline phase may increase the activation energy of mobility. However, the study in [3] does not discuss the problems of mobility of defects determined by diffusion: in volume, along the boundaries, etc.

The diffusion mechanisms of creep imply that in a field of heterogeneous mechanical stresses, local diffusion flows arise between vacancy sources and vacancy outlets, which

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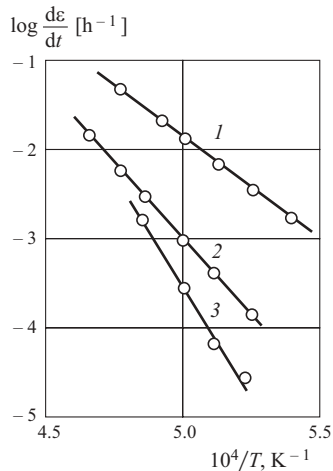
Fig. 1. Creep $d\varepsilon/dt$ in corundum ceramics at pressure of 1.3 MPa. Prevailing crystal size: *1*) 10 μm (sample 1), *2*) 30 μm (sample 2); *3*) 40 μm (sample 3).

are boundaries between structural elements. The creep rate in this case is limited by the slowest process; in most cases that is the speed of migration of vacancies inside a volume until reaching the boundaries, whose diffusion permeability is significantly higher. In disperse structures with the size of a structural element below $10^{-3} - 10^{-4}$ cm, the number of lattice points in a purely volume state is insignificant, and boundary diffusion becomes active.

The present study continues a research started in [3] and considers the role of a grid of crystal boundaries in creep, or more exactly, the role of boundary zones, in which diffusion is determined by the boundary diffusion coefficient D_b. At the same time, it is assumed that mass transfer outside the boundary zones in densely sintered polycrystalline ceramics is controlled by the volume diffusion coefficient D_{vol}. This representation is based on an experimenter's approach, i.e., a correlation of theoretical concepts with experimental data.

A mechanism of diffusion controlled by diffusion along the crystal boundaries was proposed by Cobble [6] and nearly coincides with the volume diffusion mechanism [7]. The difference consists in the inverse proportion of the creep rate to the cube of the size of a crystal (in volume diffusion, it is inversely related to the square of the size of a crystal). A consecutive analysis of diffusion creep taking into account both volume and boundary diffusions is carried out in [8]. The analysis also takes into account the conditions of compatibility at the crystal boundaries taking into account the need of slipping along the boundaries and the existence of shorter diffusion pathways along the boundaries. The expressions for the creep rate have the following form:

for the volume diffusion mechanism

$$\frac{d\varepsilon}{dt} = \frac{\alpha_1 D_{vol} \Omega \sigma}{kTl^2} \, ;$$

for the boundary diffusion mechanism

$$\frac{d\varepsilon}{dt} = \frac{\alpha_2 D_b \Omega \sigma}{kTl^3} \, ,$$

where ε is the deformation; t is the time; α_1 and α_2 are coefficients; D_{vol} and D_b are the coefficients of volume diffusion and diffusion along crystal boundaries; Ω is the atomic volume; σ is the applied stress; k is the Boltzmann constant; T is the temperature; l is the crystal size, i.e., the distance between vacancy outlets and sources; and δ is the width of a boundary.

Assuming that the volume and the boundary mass flows are additive, the effective diffusion coefficient in the general case will be

$$D_{ef} = D_{vol} \left(1 + \frac{D_b \delta}{D_{vol} l} \right).$$

With $l \ll l_{cr}$ and $D_{ef} \approx D_b \delta / D_{vol}$, the boundary diffusion mechanism proposed by Cobble will prevail, and vice versa, when $l \gg l_{cr}$, volume diffusion will prevail. It should be noted that the notions of the "width of a boundary" and "size of a crystal" for real materials are rather indefinite and sometimes cannot be numerically expressed correctly enough. For instance, in bimodal distribution of crystals by sizes, a certain "effective" size ought to be determined. The width of a boundary in creep may continously vary due to the diffusion of impurities toward the boundary or, on the contrary, dissolution of impurities in the volume, etc.

Similarly to [3], the present paper discusses experimental data on creep in densely sintered polycrystalline oxide ceramics of the technical-purity grade. The conditions of the experiments and the operations involved in the preparation of samples are described in [3]. The concentration of thermal vacancies is insignificant and has virtually no effect on deformation in such materials; therefore, the rate and the activation energy of the process are determined by impurity and nonstoichiometric defects, whose formation can be described in the context of the quasichemical approach [4, 5].

The state of a grid of boundaries and the size and shape of crystals are determined by the whole prehistory of the manufacture of ceramics. The final fixing of a material structure occurs in firing. During this technological operation, pores are removed from an intermediate porous product, and crystals grow at the final stage of firing [9]. In the course of crystal growth, the volume is purified from impurities and micropores, which become concentrated near the boundaries, and the density of dislocations decreases. In analyzing the behavior of ceramics under the effect of mechanical stresses it is significant that the concentration and mobility of vacancies are modified, as well as the diffusion path from a vacancy source to an outlet.

Figure 1 shows the temperature dependence of the creep rate for corundum samples obtained in different firing condi-
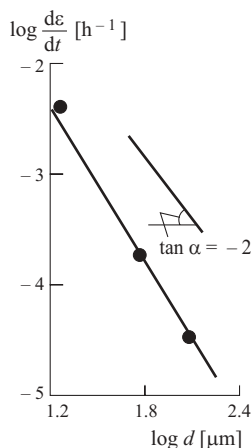
Fig. 2. Creep rate $d\varepsilon/dt$ in samples depending on the size of crystals at temperature 1650°C and pressure of 1.3 MPa.

Fig. 3. Creep $d\varepsilon/dt$ in corundum ceramics at pressure of 1.3 MPa. Prevailing crystal size: *1*) $20 - 30$ μm; *2*) $40 - 50$ μm.

Fig. 4. Creep $d\varepsilon/dt$ in ceramic samples of periclase – aluminomagnesia spinel system at pressure of 0.6 MPa. Estimated mass content of spinel: *1*, *2*, *3*, *4*, *5*, *6*, *7*, and *8*) 0; 5.0; 10.0; 20.0; 55.0; 77.7; 87.5; and 100%, respectively.

tions. Samples 1 and 2 were fired in a oxidizing atmosphere at the maximum temperature 1730°C with respective exposures 2 and 16 h, and sample 3 was fired in vacuum at 1800°C for 2 h. Judging from the petrographic data, the sizes of crystals are as follows: sample 1 — the prevailing size 10 μm and the maximum size 20 μm, sample 2 — 30 and 60 μm, sample 3 — 40 and 120 μm, respectively. Samples 1 and 2 consist of rather isometric crystals, and sample 3 consists of elongated crystals. It can be seen that with increasing size of crystals, the creep rate for a given temperature and load drops, and this dependence is nearly inversely proportional to the square of the size of crystals (Fig. 2), which indicates the prevalence of volume diffusion. At the same time, the activation energy of creep increases from 420 to 780 kJ/mole, which can be accounted for by two factors: a diminished effect of boundary diffusion and a decreased role of the impurity centers, since the impurities become concentrated at the boundaries in recrystallization. As shown by evaluations quoted in [9], boundary diffusion in metals prevails only in the case of very disperse structures with a typical size of about 10^{-3} cm or smaller. Most probably, the process in this case is controlled by the volume diffusion of vacancies formed as a consequence of the existence of impurity centers.

Similar results were obtained for periclase ceramics (Fig. 3). Samples were oxidized in an oxidizing atmosphere at temperatures 1650°C (prevailing crystal size $20 - 30$ μm) and 1700°C ($40 - 50$ μm) with 2 h exposure. The rate of deformation of ceramics under the given temperature and load is inversely proportional to the square of the size of crystals, and the activation energy is 340 and 440 kJ/mole, respectively.

Thus, high-temperature deformation in densely sintered oxide ceramics of the technical-purity grade is limited by the volume diffusion of vacancies, whereas the role of boundary diffusion is insignificant and manifested only in fine-crystalline materials. As the crystals grow, the diffusion pathway of vacancies from sources to outlets increases and the vacancy concentration decreases due to the approach of impurities to
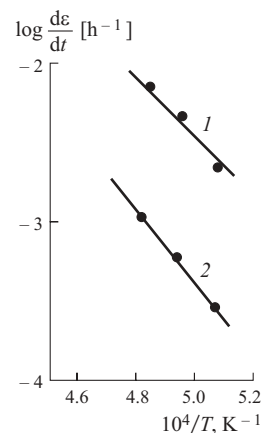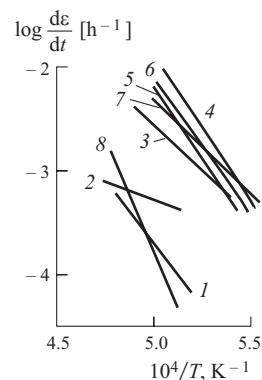
the boundaries. Accordingly, as the size of the crystals increases, the creep rate drops, and the activation energy of creep grows. It can be assumed that at initial stages of recrystallization in sintering (i.e., with relatively small sizes of crystals), the boundaries migrate comparatively quickly due to a substantial motive force, namely, the boundary curvature [9]. This process is characterized by a high degree of nonequilibrium, and the volume of a crystal has excessive free energy due to a substantial content of nonequilibrium substructure defects (vacancies, impurities, dislocations). Therefore, while sizes of crystals are small, the activation energy of diffusion is relatively low. As the size of the crystals increases, the boundary curvature decreases, the process becomes more equilibrium, the excessive free energy decreases, and the activation energy of creep increases.

Figure 4 shows the temperature dependence of the creep rate in ceramics for the periclase – aluminomagnesian spinel system. It is known [10] that the components of this system form a eutectic with a melting point around 2000°C for a magnesium oxide content of 45 wt.%, and solid solutions exist in the ranges adjacent to the pure components. The structure of medium compositions is a eutectic mixture of periclase and spinel crystals. The formation of defects in the context of the quasichemical approach and their role in creep are discussed in [3] for ceramics of the specified system. It is essential for the present study that a virtually equally ex-
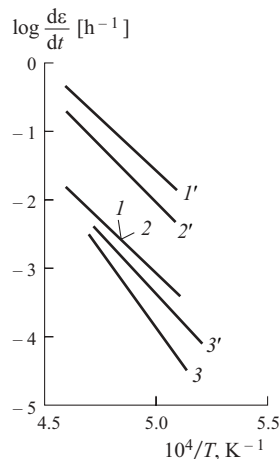
Fig. 5. Creep $d\varepsilon/dt$ at pressure of 2.5 MPa in initial (*1*) corundum ceramic samples and samples after thermal aging for 10 h at a temperature of 1800°C (*2*) and 1900°C (*3*); *1'*, *2'*, *3'*) the same but with a 0.5% magnesium oxide additive.
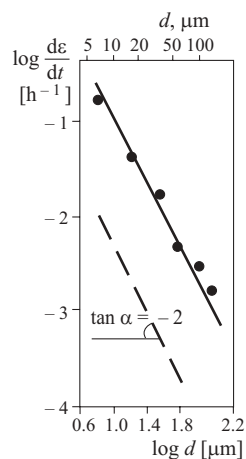

Fig. 6. Creep rate $d\varepsilon/dt$ in the considered corundum ceramic samples and samples with a 0.5% MgO additive depending on the size of crystals at 1750°C and pressure of 1.3 MPa.

purity centers, namely, a constant number of anion vacancies, by the following reaction:

$$2MgO \rightarrow 2Mg'_{Al} + V_O^{\bullet\bullet} + 2O_O^x.$$

This shifts the Schottky equilibrium of internal disordering to the left

$$0 \rightarrow 2V'''_{Al} + 3V_O^{\bullet\bullet}$$

and delays the diffusion processes. In particular, the rate of removal of pores and the rate of growth of crystals in the course of sintering and subsequent thermal aging decrease [10]. The existence of a certain quantity of impurity centers gives rise to a constant creep activation energy [3] in accordance with the energy of the reactions of impurity-center formation. The concentration of these centers and the length of a diffusion path from a vacancy source to an outlet (i.e., the size of a crystal) determine the creep rate.

Such behavior of samples can be accounted for by the segregation of aluminomagnesia spinel at the boundaries of the corundum crystals. It is known that spinel virtually does not get dissolved in corundum [11], which blocks the sources (outlets) of vacancies. Furthermore, it is possible that the magnesium cation acts as a buffer ensuring a constant concentration of vacancies, since it can either take the place of aluminum ion or pass into an interstice:

$$3MgO \rightarrow 2Mg'_{Al} + Mg_i^{\bullet\bullet} + 3O_O^x.$$

On the other hand, samples even after aging consist of relatively small crystals with excessive energy and a low activation energy of mobility. However, such behavior of ceramics with an additive means that these materials should exhibit a sharp modification (not of the Arrhenius type) of viscosity in the range of pre-melting temperatures. It is worth noting that the creep rate of the samples with an additive at remote stages of aging (i.e., relatively large-crystalline samples, dependence *3'* in Fig. 5) approximately correlates with the creep rate of large-crystalline samples without an additive. This phenomenon, in our opinion, requires a further clarification in view of a shortage of experimental data. Possibly, special experiments are needed to clarify the mechanism of this phenomenon.

The creep rate and the activation energy of creep in samples without additives depend on the distribution of a random set of impurities and their segregation during the crystal growth in heat treatment. The approach of the impurities to the boundary and the growth of crystals decrease the concentration of impurities in the volume and extend the diffusion pathway of vacancies from a source to an outlet. These processes produce a decrease in the creep rate and an increase in the creep activation energy [3]. For fine-crystalline structures with a crystal size of about 10^{-3} cm a certain increase in ac-

tended grid of boundaries in medium compositions adjacent to the eutectic one gives rise to a constant creep rate. This shows that deformation in these materials is determined by the behavior of the lowest-melting and finest-crystalline part of the microstructure.

A repeated effect of high temperatures leads to a further modification of the material structure, i.e., thermal aging of these materials. This process is actually a continuation of the final stage of sintering: the crystals continue growing, the impurities reach the boundaries, while the latter become wider, and micropores are removed [11, 12]. All this occurs simultaneously, and it appears impossible to take into account a separate effect of each separate factor.

Experimental data (Fig. 5) show that an increase in the size of crystals in aging does not qualitatively modify the behavior of corundum ceramics: similarly to the results shown in Fig. 1, the creep rate drops, and the activation energy grows up to 880 kJ/mole. However, an introduction of 0.5 wt.% MgO sharply changes the situation: whereas the creep rate decreases, the activation energy virtually does not change and amounts to around 590 kJ/mole.

According to the quasichemical approach, the introduction of a MgO additive in Al_2O_3 leads to the formation of im-

tivation energy is possibly related as well to a decrease in the role of surface diffusion.

Figure 6 shows the dependence of the creep rate in the considered samples of corundum ceramics and in samples with a 0.5 wt.% MgO additive on the size of crystals. It is worth noting that all points fall on the same rectilinear dependence in the selected coordinates. This shows that the additive does not qualitatively modify the diffusion mechanism (slope ≈ 2) of the process. According to the concepts discussed in [3, 4], creep is controlled by self-diffusion occurring in the corundum lattice, whereas the cell size of the grid of boundaries determines the length of a pathway from a vacancy source to an outlet and, accordingly, the rate of diffusion. The quantity and the distribution of impurities and additives, despite their low total content, determine the process activation energy and to some extent modify the rate of the process rate.

It should be noted that the notion of the "size of crystals" in the case of corundum ceramics with clearly nonisometric crystals is very indefinite, since their size distribution is bimodal or, more often, plateau-shaped (especially in large-crystalline materials). Calculations performed using a special method [13] demonstrated that the effective petrographic size of crystals valid in creep is closer to a maximum size than to a medium size (distribution curve median). In the construction of dependences similar to those indicated in Fig. 6a the ratio between sizes is actually taken into account. It is possible that the ratio between the maximum sizes is closer to the ratio of effective crystal sizes than the ratio of medium sizes is. It can also be assumed that self-coordinated deformation of an ensemble of crystals different in sizes proceeds in the following way. Fine crystals, which have a higher creep rate, soon get deformed, and resistance is mainly offered by large crystals. This follows from the kinetic laws: the speed of a sequence of consecutive processes is limited by the speed of its slow stage. When crystals are extended in a certain direction, the length of a diffusion path of vacancies physically extended in this direction increases.

As in other processes described by an Arrhenius-type function [4, 14, 15], the pre-exponential member S (called the structural factor) in the dependence of the creep rate $d\varepsilon/dt$ on temperature T,

$$\frac{d\varepsilon}{dt} = S \exp\left(-\frac{Q}{RT}\right),$$

where R is the gas constant, is related to the activation energy Q (Fig. 7). This empirical rule was named the "compensation effect." Numerous mechanisms have been proposed to account for this effect (one of them is described in [4]), but a sufficiently strict theory does not yet exist. It is also thought that this effect does not have a physical nature, but a mathematical nature, and this relationship is implied in the Arrhenius equation. [15].
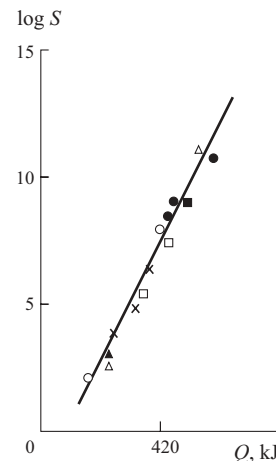

Fig. 7. Dependence of structural factor S on activation energy of creep Q: $\bullet$) $MgO \cdot Al_2O_3$; $\times$) CeO_2; $\triangle$) $3Al_2O_3 \cdot 2SiO_2$; $\square$) MgO; $\circ$) Al_2O_3; $\blacksquare$) ZrO_2; $\blacktriangle$) Sc_2O_3.

Consequently, the rate of high-temperature creep in densely sintered oxide-based ceramics is determined by the concentration and mobility of vacancies. The role of a crystal boundary grid consists in the fact that its cell size (i.e., the crystal size) determines the length of the diffusion path of vacancies from a source to a boundary, which is a vacancy outlet of virtually infinite power. The effective crystal size in creep is closer to a maximum one than to a medium size petrographically measured. The vacancy concentration in ceramics of the technical-purity grade is determined by the contribution of the total amount of impurities and technological additives and their distribution in the volume of a material. In particular, the redistribution of impurities and their approach to a boundary during the growth of crystals under firing and thermal aging has a significant effect on the creep rate and the activation energy. The diffusion mobility of vacancies in standard relatively large-crystalline ceramics (size of crystals about 10 μm or more) is determined by the volume diffusion coefficient, and the role of boundary diffusion becomes perceptible when the sizes of crystals is smaller.

Thus, by regulating the cell size of a grid of boundaries it is possible to modify creep in ceramics and to obtain materials with preset properties. For instance, the most creep-resistant products should have a large-crystalline structure.

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